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Crystal Structures of Analogues of D-Galactose. IV.* 1,2,3,6-Tetra-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-*α*-D-galactopyranose

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Abstract

$C_{28}H_{38}O_{19}$, $M_r = 678\cdot60$, is triclinic, space group $P1$, with $a = 10\cdot7141\,(8)$, $b = 11\cdot1690\,(11)$, $c = 8\cdot0839\,(8)$ Å, $\alpha = 102\cdot19\,(1)$, $\beta = 98\cdot59\,(1)$, $\gamma = 65\cdot77\,(1)°$, $V = 860\cdot1\,(1)$ Å^3, $Z = 1$, $F(000) = 358$, $D_x = 1\cdot310$ Mg m^{-3}. The structure was refined with two sets of data to $R = 0\cdot052$, $R_w = 0\cdot056$, for the Mo set (2351 reflexions), and to $R = 0\cdot070$, $R_w = 0\cdot074$, for the Cu set (2779 reflexions). The anomeric parts have the following bond distances: α moiety, C(5′)–O(5′) = 1·436, O(5′)–C(1′) = 1·395, C(1′)–O(1′) = 1·446, O(1′)–C(11′) = 1·358 Å; β moiety, C(5)–O(5) = 1·427, O(5)–C(1) = 1·420, C(1)–O(1) = 1·387, O(1)–C(4′) = 1·435 Å. The glycosidic link has an angle C(1)–O(1)–C(4′) of 115·0°. Both rings have the usual distorted chair conformation and may be considered twisted by 44° from each other. The galactoside substituents present a difference of 96° in the angle of twist at the point of attachment to the ring.

Introduction

The present study is part of a project of research on sugar compounds with biological interest (Chacon-Fuertes & Martín-Lomas, 1975). The *β*1–3 compound has already been studied (Foces-Foces, Cano & García-Blanco, 1980), and we now describe the *β*1–4 D-galactoside.

Structure solution

As the solution with Mo data seemed difficult, we decided to collect a new set of data with Cu radiation.

Table 1 presents additional crystal data, experimental data and details of the solution and refinement

Table 1. *Crystal-analysis parameters for* $C_{28}H_{38}O_{19}$ *at room temperature*

(*a*) Additional crystal data

Crystal size and habit: 0·30 × 0·30 × 0·17 mm; transparent, parallelepipedic, bevelled

Unit-cell determination: least-squares fit from 82 reflections; settings with $\theta < 22°$

(*b*) Experimental data collected with Mo and Cu radiations

Technique: four-circle Philips PW 1100 diffractometer; bisecting geometry

Orientation: $(0k0)$ with $\chi \sim -2°$, $\varphi \sim 108°$; $(h0h)$ with $\chi \sim 78°$, $\varphi \sim 354°$

Monochromator: graphite, oriented; Mo $K\bar{\alpha}$ ($\lambda = 0\cdot71069$ Å) and Cu $K\bar{\alpha}$ ($\lambda = 1\cdot5418$ Å)

Collection mode: ω–2θ up to $\theta = 27°$ (Mo) and 65° (Cu); scan width 1·3°; detector windows 1° × 1°; 1 min/reflection

Number of independent data: equalized for both radiations to 2927 data

Number of observed data: $I > 2\sigma(I)$; 2351 (Mo) and 2779 (Cu)

Stability: two standards monitored every 90 min; no variation detected

Absorption μ(mm^{-1}): 0·103 (Mo), 0·907(Cu); not corrected

(*c*) Solution and refinement

Solution mode: Cu data; *MULTAN* 78 system with seven reflections per non-H atoms and *K*-curve

Least-squares refinement mode: on *F*'s; only observed used; eight blocks; mixed thermal mode with H atoms isotropic; final ⟨shift/error⟩ = 0·52 (Cu), 0·50 (Mo); XRAY 70

Parameters: number of variables = 538, degrees of freedom: 1813 (Mo) and 2241 (Cu); ratio of freedom = 4·4 (Mo) and 5·2 (Cu)

Weighting scheme: empirical fit to give no trends in $\langle w\Delta^2\rangle$ *vs* $\langle F_o\rangle$ or $\langle \sin\theta/\lambda\rangle$

Thermal values: had to be fixed for H atoms isotropic corresponding to the bonded carbons, maximum values for the extremes of substituents: U_{11}[O(7)] = 0·333, U_{11} [O(8)] = 0·212, U_{33} [O(7′)] = 0·306, U_{11} [O(8′)] = 0·236 Å^2

ΔF synthesis: to give all H atoms; final with residues less than 0·28 e Å^{-3} (Cu) and 0·22 e Å^{-3} (Mo)

R and R_w (final): 0·052 and 0·056 (Mo), 0·070 and 0·074 (Cu)

Absolute configuration: not determined; the one displayed was already known from chemical synthesis; no anomalous-dispersion correction applied

Atomic scattering factors: from *International Tables for X-ray Crystallography* (1974)

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* Part III: Foces-Foces, Cano & García-Blanco (1980).

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together with the programs used on a Univac 1100: *MULTAN* 78 (Main, Lessinger, Woolfson, Germain & Declercq, 1978) and XRAY 70 (Stewart, Kundell & Baldwin, 1970).*

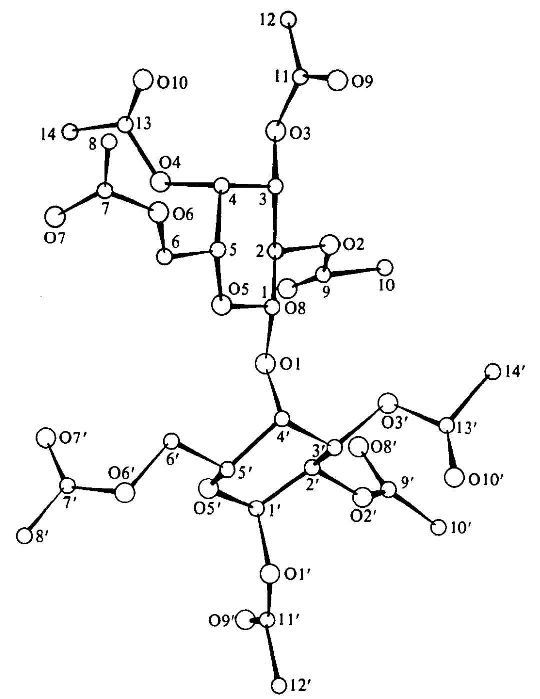

Fig. 1. A perspective view of the molecule with the atom numbering.

Results

A view of the molecule with the atom numbering is presented in Fig. 1. Fig. 2 presents the results of normal probability analyses (Abrahams & Keve, 1971) used for comparing data and results: (*A*) and (*B*) show the consistency of the weighting schemes used, (*C*) the agreement between both sets of data with the weighting scheme used, (*D*) and (*E*) the agreement between both sets of derived coordinates and thermal factors. The slopes were used for the weighted average in Tables 2 and 3. Finally (*F*) compares the two sets of derived distances up to 3·5 Å and (*G*) compares derived distances for the α and β moieties.

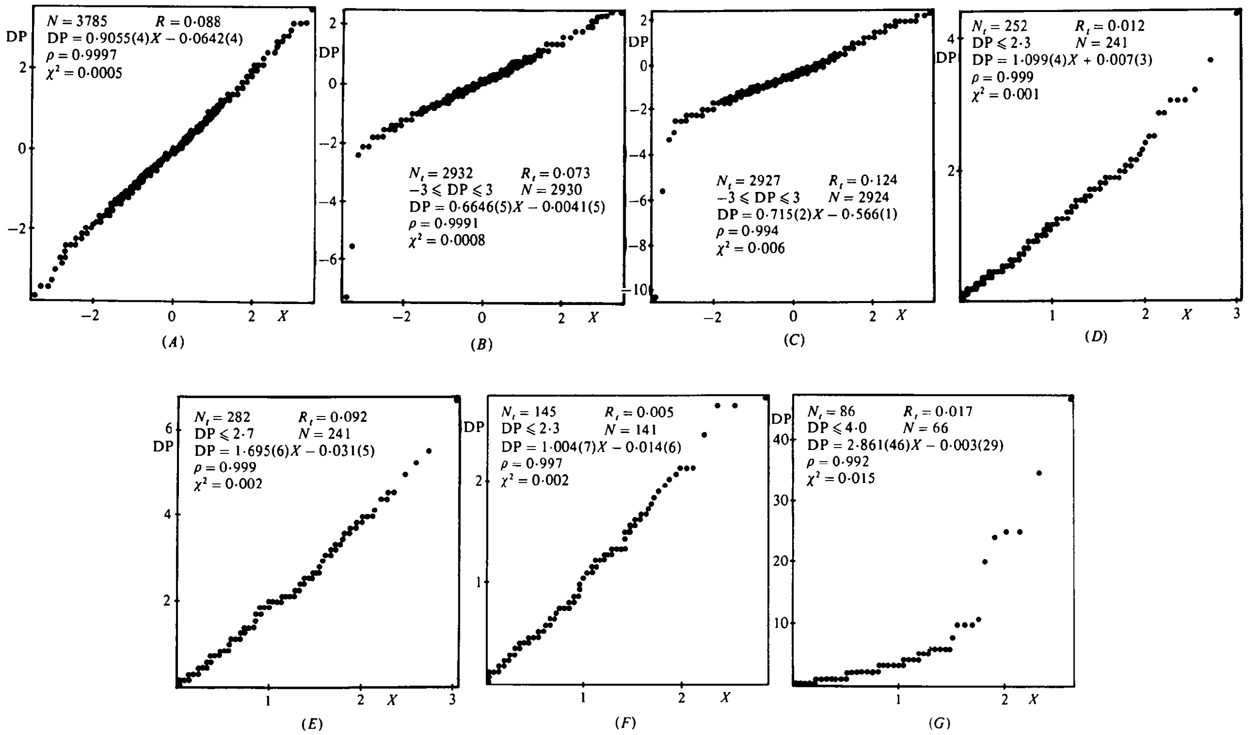

Fig. 2. Normal probability plots for the comparison of both data and results sets: (*A*) δR(Mo) plot: DP = $(F_c-F_o)/(w)^{-1/2}$; (*B*) δR(Cu) plot: DP = $(F_o-F_c)/(w)^{-1/2}$; (*C*) Cu *vs* Mo plot: DP = $(F_{o1}-F_{o2})/(1/w_1 + 1/w_2)^{1/2}$; (*D*) Cu *vs* Mo plot: DP = $|r_1-r_2|/(\sigma_1^2 + \sigma_2^2)^{1/2}$ (H atoms included); (*E*) Cu *vs* Mo plot: DP = $|U_1-U_2|/(\sigma_1^2 + \sigma_2^2)^{1/2}$ (H atoms not included); (*F*) Cu *vs* Mo plot: DP = $|d_1-d_2|/(\sigma_1^2 + \sigma_2^2)^{1/2}$ (H atoms not included) (*d* up to 3·5 Å); (*G*) α *vs* β plot: DP = $|d_1-d_2|/(\sigma_1^2 + \sigma_2^2)^{1/2}$ (H atoms not included) (*d* up to 3·5 Å) (weighted values and σ's × 1·099).

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* Lists of structure factors, fractional coordinates and thermal parameters for the Mo and Cu data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35997 (59 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Mo–Cu *weighted atomic coordinates* ($\times 10^4$) *and the equivalent isotropic temperature factors* ($\times 10^3$) *with their pooled e.s.d.'s multiplied by* $k = 1\cdot099$ *or* $1\cdot695$ *respectively*

$$r = \left(\frac{1}{\sigma^2\,\mathrm{Cu}}\,r_{\mathrm{Cu}} + \frac{1}{\sigma^2\,\mathrm{Mo}}\,r_{\mathrm{Mo}}\right)\bigg/\left(\frac{1}{\sigma^2\,\mathrm{Cu}} + \frac{1}{\sigma^2\,\mathrm{Mo}}\right);$$

$$\sigma(r) = k/(1/\sigma^2_{\mathrm{Cu}} + 1/\sigma^2_{\mathrm{Mo}})^{1/2}.$$

	x	y	z	U_{eq} (Å^2)
C(1)	4951 (4)	5695 (4)	6758 (6)	68 (2)
O(1)	5681	5522	8319	67 (1)
C(2)	3430 (4)	6246 (4)	7025 (5)	64 (2)
O(2)	3099 (3)	5241 (3)	7499 (4)	73 (2)
C(3)	2621 (3)	6577 (4)	5351 (5)	63 (2)
O(3)	1192 (2)	7180 (3)	5643 (4)	68 (1)
C(4)	3015 (4)	7532 (4)	4676 (5)	64 (2)
O(4)	2613 (3)	8772 (3)	5836 (3)	64 (1)
C(5)	4562 (4)	6953 (4)	4547 (6)	67 (2)
O(5)	5248 (3)	6647 (3)	6152 (4)	74 (2)
C(6)	5084 (5)	7923 (5)	4142 (7)	81 (3)
O(6)	4515 (4)	8200 (4)	2484 (4)	91 (2)
C(7)	4418 (7)	9281 (7)	2073 (7)	100 (4)
O(7)	4687 (10)	10100 (6)	3046 (7)	191 (7)
C(8)	3846 (15)	9434 (10)	290 (10)	146 (8)
O(8)	3116 (5)	6178 (5)	10234 (5)	107 (3)
C(9)	2951 (5)	5342 (5)	9173 (7)	85 (3)
C(10)	2526 (11)	4255 (10)	9398 (11)	123 (5)
C(11)	332 (4)	6922 (4)	4374 (5)	70 (2)
O(9)	728 (4)	6171 (5)	3107 (5)	117 (3)
C(12)	−1126 (5)	7733 (6)	4734 (7)	89 (3)
C(13)	1559 (5)	9833 (4)	5350 (6)	81 (2)
C(14)	1204 (7)	10973 (6)	6749 (10)	104 (3)
O(10)	981 (6)	9812 (4)	3978 (6)	148 (3)
C(1′)	7886 (5)	4747 (5)	11814 (6)	81 (3)
O(1′)	9324 (3)	3875 (4)	11901 (4)	85 (2)
C(2′)	7070 (4)	3935 (5)	10937 (6)	75 (2)
O(2′)	7463 (4)	2765 (4)	11675 (5)	91 (2)
C(3′)	7335 (4)	3470 (4)	9076 (5)	69 (2)
O(3′)	6393 (3)	2853 (3)	8321 (4)	77 (2)
C(4′)	7097 (4)	4630 (4)	8238 (6)	69 (2)
C(5′)	7993 (4)	5346 (5)	9185 (7)	78 (2)
O(5′)	7703 (3)	5766 (3)	10941 (5)	87 (2)
C(6′)	7759 (6)	6570 (6)	8445 (11)	108 (4)
O(6′)	8908 (4)	6967 (4)	9068 (6)	103 (2)
C(7′)	8586 (5)	8215 (6)	9676 (8)	96 (3)
O(7′)	7435 (5)	8984 (6)	9783 (11)	179 (7)
C(8′)	9825 (8)	8539 (8)	10135 (10)	112 (5)
C(9′)	6602 (9)	2705 (6)	12656 (8)	113 (6)
O(8′)	5538 (9)	3615 (5)	12991 (10)	192 (9)
C(10′)	7183 (12)	1401 (10)	13245 (12)	143 (7)
C(11′)	9982 (6)	3700 (6)	13457 (8)	101 (4)
C(12′)	11482 (11)	2919 (15)	13281 (15)	144 (6)
O(9′)	9407 (6)	4143 (7)	14742 (7)	143 (4)
C(13′)	6887 (5)	1585 (5)	7632 (6)	84 (3)
O(10′)	8102 (5)	937 (4)	7496 (7)	124 (3)
C(14′)	5791 (8)	1071 (9)	7107 (11)	117 (4)

From the weighted averaged coordinates, bond distances (Table 4), bond angles (Table 5) and torsion angles (Table 6) were calculated. Asterisks mark the distances which are considered significantly different in plot (*G*).

Table 3. Mo–Cu *weighted atomic coordinates* ($\times 10^3$) *with their pooled e.s.d.'s multiplied by* $1\cdot099$ *for the* H *atoms with bond distances in* Å

$$r = \left(\frac{1}{\sigma^2\,\mathrm{Cu}}\,r_{\mathrm{Cu}} + \frac{1}{\sigma^2\,\mathrm{Mo}}\,r_{\mathrm{Mo}}\right)\bigg/\left(\frac{1}{\sigma^2\,\mathrm{Cu}} + \frac{1}{\sigma^2\,\mathrm{Mo}}\right);$$

$$\sigma(r) = 1\cdot099/(1/\sigma^2_{\mathrm{Cu}} + 1/\sigma^2_{\mathrm{Mo}})^{1/2}.$$

	x	y	z	C–H
H(1)	522 (5)	483 (5)	597 (7)	1·00 (5)
H(2)	319 (6)	701 (6)	795 (7)	0·98 (5)
H(3)	277 (6)	566 (6)	452 (7)	1·07 (6)
H(4)	261 (6)	755 (5)	352 (7)	0·97 (5)
H(5)	493 (6)	608 (6)	364 (7)	1·05 (5)
H(6*a*)	606 (7)	749 (6)	417 (8)	0·95 (6)
H(6*b*)	459 (6)	849 (6)	510 (8)	0·96 (6)
H(8*a*)	286 (10)	940 (9)	37 (11)	1·09 (11)
H(8*b*)	427 (11)	871 (10)	−15 (13)	0·79 (9)
H(8*c*)	380 (9)	1024 (9)	−6 (11)	0·98 (11)
H(10*a*)	262 (11)	358 (11)	839 (14)	0·97 (10)
H(10*b*)	217 (12)	428 (11)	1041 (13)	0·94 (12)
H(10*c*)	331 (11)	342 (11)	972 (14)	1·02 (10)
H(12*a*)	−115 (7)	855 (7)	516 (9)	0·89 (8)
H(12*b*)	−123 (7)	724 (7)	571 (9)	1·10 (9)
H(12*c*)	−170 (7)	787 (7)	385 (9)	0·87 (7)
H(14*a*)	188 (8)	1108 (8)	714 (9)	0·79 (9)
H(14*b*)	57 (8)	1107 (8)	756 (10)	0·97 (9)
H(14*c*)	57 (8)	1171 (8)	633 (10)	0·92 (7)
H(1′)	768 (6)	517 (6)	1293 (8)	0·94 (6)
H(2′)	620 (6)	452 (6)	1115 (7)	0·91 (5)
H(3′)	827 (6)	279 (5)	902 (7)	0·98 (5)
H(4′)	731 (6)	437 (6)	690 (7)	1·09 (6)
H(5′)	903 (7)	481 (7)	916 (8)	1·03 (6)
H(6′*a*)	684 (8)	733 (8)	889 (10)	1·06 (7)
H(6′*b*)	754 (8)	660 (8)	718 (10)	1·02 (8)
H(8′*a*)	970 (8)	948 (8)	1052 (10)	0·98 (9)
H(8′*b*)	1048 (8)	824 (8)	934 (10)	0·93 (9)
H(8′*c*)	1005 (9)	832 (9)	1092 (11)	0·70 (9)
H(10′*a*)	724 (14)	76 (13)	1248 (17)	0·83 (12)
H(10′*b*)	795 (13)	111 (12)	1410 (17)	0·98 (12)
H(10′*c*)	660 (15)	123 (14)	1372 (17)	0·88 (18)
H(12′*a*)	1194 (9)	297 (9)	1233 (12)	1·00 (12)
H(12′*b*)	1165 (10)	210 (9)	1323 (12)	0·85 (11)
H(12′*c*)	1188 (10)	277 (10)	1413 (13)	0·76 (10)
H(14′*a*)	517 (10)	171 (10)	655 (12)	0·91 (10)
H(14′*b*)	597 (10)	34 (10)	622 (12)	1·00 (15)
H(14′*c*)	491 (10)	140 (10)	738 (12)	0·94 (18)

Discussion

A. Molecular constitution

A.1. *The anomeric moieties and the glycosidic link.* For the present (*β*1–4) compound the *β* moiety has bond lengths and angles in agreement with the literature values (Table 7, other *β*-pyranoses in Foces-Foces, Cano & García-Blanco, 1980) but they are different from those in the *β*1–3 compound where they present a more symmetric distribution. This fact includes the glycosidic link.

The *α* moiety has an acetal sequence analogous to that in the *β*1–3 compound, both being different from that predicted from the literature, as the C(1′)–O(1′)–C(11′) part is more like the acetyl substituents.

The only difference is that C(11′) is more symmetrically situated with respect to the ring in the present compound. This situation is characterized by the torsion angles O(5′)—C(1′)—O(1′)—C(11′) = 121·7 and C(2′)—C(1′)—O(1′)—C(11′) = −116·5°, while these values for the β1–3 molecule were 83·1 and −156·4° respectively.

*A.*2. *The non-anomeric parts.* Ranges for the lengths and angles are given in Table 7. All C—C bonds are alike, whether within the ring or in the substituents. Excluding the acetyl bonds, the C—O distances have a quite wide range, 9·8σ. But if we exclude the three anomeric bonds, C(1)—O(5), C(1)—O(1) and C(1′)—O(5′), plus the acetyl value for O(1′)—C(11′), the eleven other bonds have an acceptable range of 3·7σ.

Table 4. *Bond distances* (Å) *from the weighted coordinates, with the corresponding e.s.d.'s in parentheses*

For completeness some values have been repeated. Asterisks mark the values flagged as different by the half-normal probability plot between moieties.

α Moiety		β Moiety	
Non-anomeric moiety			
C(1′)—C(2′)	1·512 (8)	C(1)—C(2)	1·519 (5)
C(2′)—C(3′)	1·514 (7)	C(2)—C(3)	1·522 (5)
C(3′)—C(4′)	1·500 (7)	C(3)—C(4)	1·516 (7)
C(4′)—C(5′)	1·516 (7)	C(4)—C(5)	1·524 (5)
C(2′)—O(2′)	1·429 (7)	C(2)—O(2)	1·443 (7)
C(3′)—O(3′)	1·441 (6)	C(3)—O(3)	1·431 (4)
C(4′)—O(1)	1·435 (3)	C(4)—O(4)	1·437 (4)
C(5) substituents			
C(5′)—C(6′)	1·520 (10)	C(5)—C(6)	1·515 (8)
C(6′)—O(6′)	1·462 (8)	C(6)—O(6)	1·428 (6)
Acetal sequence			
C(5′)—O(5′)	1·436 (7)	C(5)—O(5)	1·427 (5)
O(5′)—C(1′)	1·395 (7)	O(5)—C(1)	1·420 (7)
*C(1′)—O(1′)	1·446 (5)	*C(1)—O(1)	1·387 (4)
*O(1′)—C(11′)	1·358 (7)	*O(1)—C(4′)	1·435 (3)
Glycosidic link			
*C(4′)—O(1)	1·435 (3)	*C(1)—O(1)	1·387 (4)
*O(1)—C(1)	1·387 (4)	*O(1)—C(4′)	1·435 (3)
Acetyl groups			
O(2′)—C(9′)	1·332 (10)	O(2)—C(9)	1·362 (6)
O(1′)—C(11′)	1·358 (7)	O(3)—C(11)	1·340 (5)
O(3′)—C(13′)	1·317 (5)	O(4)—C(13)	1·341 (5)
O(6′)—C(7′)	1·292 (7)	O(6)—C(7)	1·279 (9)
C(9′)—O(8′)	1·196 (9)	C(9)—O(8)	1·179 (7)
C(11′)—O(9′)	1·194 (8)	C(11)—O(9)	1·187 (5)
C(13′)—O(10′)	1·212 (6)	C(13)—O(10)	1·188 (7)
C(7′)—O(7′)	1·182 (7)	C(7)—O(7)	1·177 (10)
C(9′)—C(10′)	1·482 (13)	C(9)—C(10)	1·512 (15)
C(11′)—C(12′)	1·493 (12)	C(11)—C(12)	1·486 (6)
C(13′)—C(14′)	1·479 (12)	C(13)—C(14)	1·473 (8)
C(7′)—C(8′)	1·490 (11)	C(7)—C(8)	1·496 (10)

For the C—C—C angles the wide range of 8·3σ is due to the high value at C(4)—C(5)—C(6) of 113·4°. If this is excluded the range drops to 4·4σ. If the two extreme values of 104·2 and 111·5° for the C—C—O angles are omitted, the twenty left give a range of 6·7σ which can be reduced to 4·9σ if some angles in the α moiety, namely C(2′)—C(3′)—O(3′), C(3′)—C(2′)—O(2′), C(4′)—C(3′)—O(2′) and C(4′)—C(5′)—O(5′), are excluded.

*A.*3. *The acetyl substituents and the* H *atoms.* Two kinds of C—O distances can be deduced, those involving C(6) and C(6′) being shorter.

Table 5. *Bond angles* (°) *from the weighted coordinates, with the corresponding e.s.d.'s in parentheses*

For completeness some values have been repeated. Asterisks mark the values flagged as different by the half-normal probability plot between moieties.

α Moiety		β Moiety	
Non-anomeric moiety			
C(1′)—C(2′)—C(3′)	111·4 (4)	C(1)—C(2)—C(3)	108·7 (4)
C(2′)—C(3′)—C(4′)	110·3 (4)	C(2)—C(3)—C(4)	110·6 (3)
C(3′)—C(4′)—C(5′)	108·7 (4)	C(3)—C(4)—C(5)	109·5 (4)
C(1′)—C(2′)—O(2′)	110·3 (4)	C(1)—C(2)—O(2)	109·7 (4)
C(3′)—C(2′)—O(2′)	106·7 (4)	C(3)—C(2)—O(2)	107·3 (3)
C(2′)—C(3′)—O(3′)	107·0 (4)	C(2)—C(3)—O(3)	108·2 (3)
C(4′)—C(3′)—O(3′)	110·1 (4)	C(4)—C(3)—O(3)	109·5 (3)
C(3′)—C(4′)—O(1)	108·9 (3)	C(3)—C(4)—O(4)	108·5 (3)
C(5′)—C(4′)—O(1)	109·4 (4)	C(5)—C(4)—O(4)	109·5 (3)
C(5) substituents			
C(4′)—C(5′)—C(6′)	111·5 (5)	C(4)—C(5)—C(6)	113·4 (4)
C(6′)—O(6′)—C(7′)	115·9 (5)	C(6)—O(6)—C(7)	118·8 (5)
*C(6′)—C(5′)—O(5′)	108·1 (5)	*C(6)—C(5)—O(5)	104·2 (4)
C(5′)—C(6′)—O(6′)	107·9 (5)	C(5)—C(6)—O(6)	107·3 (4)
C(4′)—C(5′)—O(5′)	110·5 (4)	C(4)—C(5)—O(5)	109·8 (4)
Acetal sequence			
C(5′)—O(5′)—C(1′)	115·2 (4)	C(5)—O(5)—C(1)	114·0 (4)
O(5′)—C(1′)—O(1′)	109·1 (4)	O(5)—C(1)—O(1)	106·7 (3)
C(1′)—O(1′)—C(11′)	118·1 (4)	C(1)—O(1)—C(4′)	115·0 (3)
C(2′)—C(1′)—O(5′)	111·5 (4)	C(2)—C(1)—O(5)	109·3 (4)
*C(2′)—C(1′)—O(1′)	108·6 (4)	*C(2)—C(1)—O(1)	109·5 (3)
Glycosidic link			
C(1)—O(1)—C(4′)	115·0 (3)	C(1)—O(1)—C(4′)	115·0 (3)
*C(3′)—C(4′)—C(5′)	108·7 (4)	*C(2)—C(1)—O(5)	109·3 (4)
*O(1)—C(4′)—C(3′)	108·9 (3)	*C(2)—C(1)—O(1)	108·5 (3)
*O(1)—C(4′)—C(5′)	109·4 (4)	*O(5)—C(1)—O(1)	106·7 (3)
Acetyl groups			
O(2′)—C(9′)—C10′)	110·1 (7)	O(2)—C(9)—C(10)	109·2 (6)
O(1′)—C(11′)—C(12′)	109·7 (7)	O(3)—C(11)—C(12)	111·7 (4)
O(3′)—C(13′)—C(14′)	110·9 (5)	O(4)—C(13)—C(14)	111·1 (5)
O(6′)—C(7′)—C(8′)	111·7 (6)	O(6)—C(7)—C(8)	113·6 (7)
O(2′)—C(9′)—O(8′)	122·3 (7)	O(2)—C(9)—O(8)	123·3 (5)
*O(1′)—C(11′)—O(9′)	123·1 (6)	*O(3)—C(11)—O(9)	122·2 (5)
O(3′)—C(13′)—O(10′)	122·6 (5)	O(4)—C(13)—O(10)	123·1 (5)
O(6′)—C(7′)—O(7′)	122·4 (7)	O(6)—C(7)—O(7)	122·5 (7)
C(10′)—C(9′)—O(8′)	127·6 (8)	C(10)—C(9)—O(8)	127·5 (6)
C(12′)—C(11′)—O(9′)	127·2 (8)	C(12)—C(11)—O(9)	126·0 (5)
C(14′)—C(13′)—O(10′)	125·5 (6)	C(14)—C(13)—O(10)	125·8 (6)
C(8′)—C(7′)—O(7′)	125·9 (7)	C(8)—C(7)—O(7)	123·8 (8)
C(2′)—O(2′)—C(9′)	118·7 (5)	C(2)—O(2)—C(9)	117·2 (4)
*C(1′)—O(1′)—C(11′)	118·1 (4)	*C(3)—O(3)—C(11)	116·6 (3)
C(3′)—O(3′)—C(13′)	119·0 (4)	C(4)—O(4)—C(13)	118·5 (4)
C(6′)—O(6′)—C(7′)	115·9 (5)	C(6)—O(6)—C(7)	118·8 (5)

Table 6. *Some torsion angles (°) from the weighted coordinates*

The corresponding e.s.d.'s are given in parentheses.

α Moiety		β Moiety	
Pyranose groups			
O(5')–C(1')–C(2')–C(3')	51·2 (5)	O(5)–C(1)–C(2)–C(3)	58·0 (4)
O(5')–C(1')–C(2')–O(2')	169·6 (4)	O(5)–C(1)–C(2)–O(2)	175·0 (3)
H(1')–C(1')–C(2')–H(2')	49 (5)	H(1)–C(1)–C(2)–H(2)	170 (5)
C(1')–C(2')–C(3')–C(4')	−53·3 (5)	C(1)–C(2)–C(3)–C(4)	−56·1 (4)
C(1')–C(2')–C(3')–O(3')	−173·1 (4)	C(1)–C(2)–C(3)–O(3)	−176·1 (3)
H(2')–C(2')–C(3')–H(3')	−175 (5)	H(2)–C(2)–C(3)–H(3)	−166 (5)
C(2')–C(3')–C(4')–C(5')	56·0 (5)	C(2)–C(3)–C(4)–C(5)	54·7 (4)
C(2')–C(3')–C(4')–O(1')	−63·1 (4)	C(2)–C(3)–C(4)–O(4)	−64·7 (4)
H(3')–C(3')–C(4')–H(4')	58 (5)	H(3)–C(3)–C(4)–H(4)	47 (5)
C(3')–C(4')–C(5')–O(5')	−57·4 (5)	C(3)–C(4)–C(5)–O(5)	−55·1 (5)
C(3')–C(4')–C(5')–C(6')	−177·7 (4)	C(3)–C(4)–C(5)–C(6)	−171·2 (4)
H(4')–C(4')–C(5')–H(5')	−61 (5)	H(4)–C(4)–C(5)–H(5)	−47 (5)
C(4')–C(5')–O(5')–C(1')	58·4 (5)	C(4)–C(5)–O(5)–C(1)	60·7 (5)
C(5')–O(5')–C(1')–C(2')	−54·6 (5)	C(5)–O(5)–C(1)–C(2)	−62·3 (5)
C(5')–O(5')–C(1')–O(1')	65·3 (5)	C(5)–O(5)–C(1)–O(1)	−179·5 (3)
C(5')–O(5')–C(1')–H(1')	173 (4)	C(5)–O(5)–C(1)–H(1)	60 (3)
Glycosidic link			
C(1)–O(1)–C(4')–C(5')	123·6 (4)	O(5)–C(1)–O(1)–C(4')	−81·5 (4)
C(1)–O(1)–C(4')–C(3')	−117·7 (3)	C(2)–C(1)–O(1)–C(4')	160·8 (3)
C(1)–O(1)–C(4')–H(4')	7 (3)	H(1)–C(1)–O(1)–C(4')	40 (3)
Substituents			
C(3')–C(2')–O(2')–C(9')	−131·8 (5)	C(3)–C(2)–O(2)–C(9)	−140·8 (4)
O(5')–C(1')–O(1')–C(11')	121·7 (5)	C(4)–C(3)–O(3)–C(11)	93·3 (4)
C(4')–C(3')–O(3')–C(13')	121·6 (4)	C(5)–C(4)–O(4)–C(13)	131·2 (4)
O(5')–C(5')–C(6')–O(6')	74·7 (6)	O(5)–C(5)–C(6)–O(6)	175·8 (4)
C(5')–C(6')–O(6')–C(7')	−131·7 (6)	C(5)–C(6)–O(6)–C(7)	157·2 (5)
C(2')–C(1')–O(1')–C(11')	−116·5 (5)		
H(1')–C(1')–O(1')–C(11')	9 (4)		
C(1')–O(1')–C(11')–C(12')	−172·5 (6)		
C(1')–O(1')–C(11')–O(9')	6·4 (9)		

Table 7. *Range of values found in the present work*

For each kind of bond (Å) or angle (°) the sequence is: type of bond or angle; [minimum value (e.s.d.), maximum value (e.s.d.)]; number of data; range in terms of the pooled e.s.d. ($\sigma^2 = \sigma_1^2 + \sigma_2^2$); average of data (e.s.d.); dispersion of the data measured as the range/(number of data)$^{1/2}$.

C–C (rings); [1·500 (7), 1·524 (5)]; 8; 2·8σ; 1·517 (2); 0·008
C–C (all); [1·500 (7), 1·524 (5)]; 10; 2·8σ; 1·517 (2); 0·008
C–O (non-anomeric); [1·427 (5), 1·462 (8)]; 11; 3·7σ; 1·436 (2); 0·011

C–C–C; [108·7 (4), 111·5 (5)]; 7; 4·4σ; 110·1 (1); 1·1
C–C–O; [107·3 (4), 110·1 (4)]; 16; 4·9σ; 108·9 (1); 0·72

C–O (acetyl – not at C6); [1·317 (5)–1·362 (6)]; 6; 1·7σ; 1·340 (2); 0·023
C–O (at C6); [1·279 (9), 1·292 (7)]; 2; 1·1σ; 1·287 (6); 0·009
C=O (acetyl); [1·177 (10), 1·212 (6)]; 8; 3·0σ; 1·190 (2); 0·012
C–C (acetyl); [1·473 (8), 1·512 (15)]; 8; 2·3σ; 1·486 (2); 0·014

O–C–C (acetyl); [109·2 (6), 111·7 (6)]; 8; 2·9σ; 111·1 (2); 0·88
O–C–O (acetyl); [122·2 (5), 123·3 (5)]; 8; 1·6σ; 122·7 (2); 0·39
C–C=O (acetyl); [123·8 (8), 127·6 (8)]; 8; 3·4σ; 126·2 (2); 1·3
C–O–C (acetyl); [115·9 (5), 119·0 (4)]; 8; 4·8σ; 117·7 (1); 1·1

C–H (rings); [0·91 (5), 1·09 (6)]; 14; 2·3σ; 1·00 (2); 0·05
C–H (methyl); [0·70 (9), 1·10 (9)]; 24; 3·1σ; 0·91 (2); 0·08

C–C–H (rings + C6); [83 (4), 122 (5)]; 22; 6·1σ; 103·3 (7); 8·3
O–C–H (rings); [105 (4), 118 (4)]; 16; 2·3σ; 109·7 (9); 3·3
C–C–H (methyl); [98 (8), 131 (7)]; 24; 3·1σ; 112 (1); 6·7
H–C–H (methyl); [62 (10), 126 (10)]; 26; 4·5σ; 116 (2); 13

The geometry involving H atoms presents analogous characteristics to the β1–3 compound.

B. Molecular conformation

*B.*1. *The rings.* Both rings have an analogous distribution of torsion angles, 10·2σ for α and 11·9σ for β. Following the Cano, Foces-Foces & García-Blanco (1977) criterion, the torsion angles can be described as $\varphi_{j\alpha}\,(-1)^j = 55{\cdot}2^\circ + 3{\cdot}3^\circ\cos(161{\cdot}0^\circ + 60^\circ j)$ and $\varphi_{j\beta}(-1)^j = 57{\cdot}8^\circ + 3{\cdot}8^\circ\cos(67{\cdot}6^\circ + 60^\circ j)$, showing the usual chair conformation for both rings. The quasisymmetry present is defined by: $\Sigma/2 = 161{\cdot}0^\circ$ for α and $\Sigma/2 = 67{\cdot}6^\circ$ for β. The nearest symmetrical values are $\Sigma_\alpha = 300^\circ$ and $\Sigma_\beta = 120^\circ$. These values give as the most relevant symmetry for the rings a mirror plane through C(2') and C(5') and a binary axis through C(3)–C(4) and O(5)–C(1). These symmetry elements separate the least and the most puckered parts in the rings.

*B.*2. *The glycosidic link.* The C(5)–O(5)–C(1)–O(1) torsion angle for the β moiety and the analogue for α of −179·5 and 65·3° respectively agree with the values given by Jeffrey (1979) of 180 and 60° for the methyl-β-D- and methyl-α-D-pyranoses. The φ-type angles [C(11')–O(1')–C(1')–O(5')/C(2')/H(1') for α and C(4')–O(1)–C(1)–O(5)/C(2)/H(1) for β] and the ψ-type ones [C(1')–O(1')–C(11')–C(12')/O(4') for α and C(1)–O(1)–C(4')–C(3')/C(5')–H(4') for β] of the vicinal atoms about the glycosidic bonds have values in the predicted range (Lemieux & Koto, 1974) for the β anomer but those for the α anomer differ due to the characteristics of the acetyl substituent.

With the same description (Cano, Foces-Foces & García-Blanco, 1979) as in the β1–3 work, the relative twist, Fig. 3, of one ring with respect to the other can be measured by the two partial twists around C(1)–O(1) and O(1)–C(4') of 39·8 and 4·3° respectively, to give

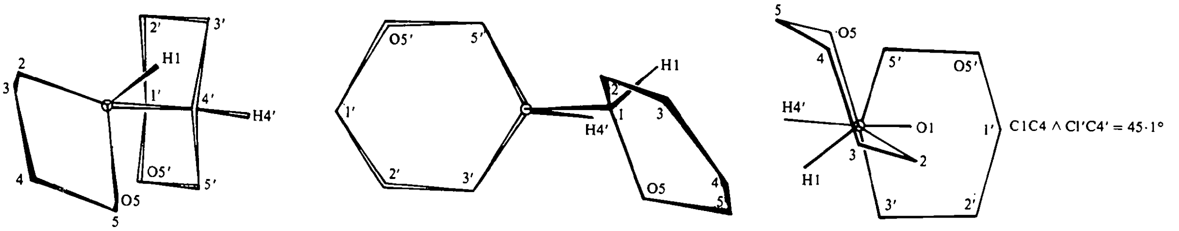

Fig. 3. The relative twist between rings through the glycosidic link.

Table 8. *Conformational characteristics and configurational angles for the ring substituents*

(*a*) Conformational characteristics of the ring substituents, with respect to the previous/next ring atom; within parentheses are values near 90°

α Angle	Conformation	β Angle	Conformation
C(1′)/C(3′)–C(2′)–O(2′)–C(9′)	(+*ac*), −*ac*	C(1)/C(3)–C(2)–O(2)–C(9)	(+*ac*), −*ac*
C(2′)/C(4′)–C(3′)–O(3′)–C(13′)	−*ac*, +*ac*	C(2)/C(4)–C(3)–O(3)–C(11)	−*ac*, (+*ac*)
C(3′)/C(5′)–C(4′)–O(1)–C(1)	−*ac*, +*ac*	C(3)/C(5)–C(4)–O(4)–C(13)	(−*ac*), +*ac*
O(5′)/C(2′)–C(1′)–O(1′)–C(11′)	+*ac*, −*ac*	O(5)/C(2)–C(1)–O(1)–C(4′)	(−*sc*), +*ap*
C(4′)/O(5′)–C(5′)–C(6′)–O(6′)	−*trans*, (+*gauche*)	C(4)/O(5)–C(5)–C(6)–O(6)	−*gauche*, +*trans*

(*b*) Configurational angles (°) for the ring substituents

Configuration angle	Substituent angle	Ring angle	β Value	α Value
ρ[C(5)–O(5)–C(1)–O(1)] =	τ[C(5)–O(5)–C(1)–O(1)] −	τ[C(5)–O(5)–C(1)–C(2)] =	−117·2 =	+119·9
ρ[O(5)–C(1)–C(2)–O(2)] =	τ[O(5)–C(1)–C(2)–O(2)] −	τ[O(5)–C(1)–C(2)–C(3)] =	+117·0 =	+118·4
ρ[C(1)–C(2)–C(3)–O(3)] =	τ[C(1)–C(2)–C(3)–O(3)] −	τ[C(1)–C(2)–C(3)–C(4)] =	−120·0 =	−119·8
ρ[C(2)–C(3)–C(4)–O(4)] =	τ[C(2)–C(3)–C(4)–O(1)] −	τ[C(2)–C(3)–C(4)–C(5)] =	−119·4 =	−119·1
ρ[C(3)–C(4)–C(5)–C(6)] =	τ[C(3)–C(4)–C(5)–C(6)] −	τ[C(3)–C(4)–C(5)–O(5)] =	−116·1 =	−120·3

a total twist of 44·1°, compared to the conformation with H(1)–C(1)–O(1)–C(4′)–H(4′) coplanar.

B.3. *The substituents.* Table 8 shows the conformation of the substituent chains. With respect to the β1–3 compound the differences are around C(1)–O(1′), C(5′)–C(6′) and C(5)–C(6). All the acetyl groups have conformations with COCO torsion angles near 0°. Around C(5′)–C(6′) and C(5)–C(6) the twists (Cano, Foces-Foces & García-Blanco, 1979) of −38·9 and 57·0° are in the opposite sense to the β1–3 compound, so they have an intrinsic rotation of about 96° one from the other.

C. Molecular configuration

No attempts have been made to determine the absolute configuration, the one displayed being known from the chemical synthesis.

D. Molecular packing

The packing ratio, volume/number of non-hydrogen atoms in the unit cell, is 18·3, in agreement with that for the packing of sugars without H bonds.

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